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Dissociative Excitation of C_2H_2 and C_2D_2 at Ne(I) Resonance Lines

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The electronically excited states of photofragments in the photolyses of C_2H_2 and C_2D_2 at neon resonance lines ($h\nu$=16.85 and 16.63 eV) were $C_2(\tilde{D}^1\Sigma_u^+, \tilde{C}^1\Pi_g, \tilde{e}^3\Pi_g, \tilde{d}^3\Pi_g)$ and CH and CD($\tilde{C}^2\Sigma^+$, $\tilde{B}^2\Sigma^-$, $\tilde{A}^2\Delta$) radicals observed by dispersing fluorescence. They are produced through a neutral superexcited state of acetylene but not *via* ionic species. A large isotope effect was observed in the emisson intensities between C_2*/CH* and C_2*/CD* ratios. The emission cross sections determined at Ne(I) lines were 2.3 Mb in both C_2H_2 and C_2D_2, indicating that about 40% of the superexcited state decomposes into the electronically excited C_2* and CH* (and CD*) radicals.

KEY WORDS: VUV photolysis/ Fluorescence/ Isotope effect/ Superexcited state/ Emission cross section/

1. INTRODUCTION

Acetylene is one of the simplest polyatomic molecules and its photochemistry has been extensively studied in a wide energy region of the exciting primary beam: below LiF cutoff (<11.8 eV)[1~6], windowless VUV (<70.85 eV)[7~17], and electron energyloss spectroscopy encompassing the range of 5–180 eV.[18~20]

The total photoabsorption cross section and the partial cross sections for the molecular and dissociative photoionization of C_2H_2 have been discussed in detail.[20] The dipole induced breakdown for the ionic photofragmentation of C_2H_2 has also been proposed in relation to the electronic states of $C_2H_2^+$ cation.[20]

At $h\nu$ <18 eV, the quantum yield of ionization (η_i) defined by the ratio of the number of ions produced to that of photons absorbed is less than unity.[3,20] The ionization yield curve shows two minima of $\eta_i \simeq 0.65$ and 0.67–0.81 at 13.5 and 16.3 eV, respectivaly[3,20], suggesting the formation of a superexcited C_2H_2** molecule which lies at the potential energy level higher than the first ionization energy and decomposes into neutral fragments without autoionization. In this work electronically excited radicals which come from VUV photodecomposition of C_2H_2 and C_2D_2 are detected by optical emission spectroscopy, and the isotope effect is reported.

2. EXPERIMENTAL

The experimental setup is identical to the one described previously.[21] In brief,

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the electronically excited radical was generated by Ne(I) (73.59 and 74.37 nm or 16.85 and 16.67 eV, respectively) irradiation. The lamp was a 10 mm inner diameter quartz tube, through which high purity neon gas (Mitsui-Toatsu Chemical Co., 99.999%) was flowed and powered by a 2.45 GHz microwave discharge. The emission spectra were observed through a quartz lens attached at right angles to the Ne(I) resonance lines, and dispersed by a Nikon G250 monochromator with a grating blazed at 250 or 500 nm. A low spectral resolution of ~6 nm was employed because of the weak emission intensity. Dispersed fluorescence was detected by a photomultiplier tube (Hamamatsu R585 or a cooled R649) and a multichannel analyzer.

The relative response of the optical system on photon energy was calibrated with a standard bromine lamp (Ushio Electronic Co., JPD-100-500CS).[22] The absolute fluorescence cross sections were determined by normalizing the fluorescence intensities of acetylene measured at 73.6 nm with that of the $CO^+(\tilde{A}^2\Pi \rightarrow \tilde{X}^2\Sigma^+)$ fluorescence, for which the fluorescence excitation spectrum has been measured up to 17.5 nm.[23]

High purity C_2H_2 and C_2D_2 were commercially purchased from Takachiho Shoji Co., and CEA in France, respectively. The minimum isotopic purity of C_2D_2 is stated to be 99 atom % and used without further purification.

3. RESULTS AND DISCUSSION

The quantum yield of ionization of C_2H_2 is shown in Fig. 1 where the data are taken from Refs. 3 and 20. The quatum yield at 16.85 eV is estimated to be 0.85, indicating the superexcited state is substantial. Figs. 2 and 3 show the dispersed fluorescence of C_2H_2 and C_2D_2 in the wavelength regions of 200–600 nm

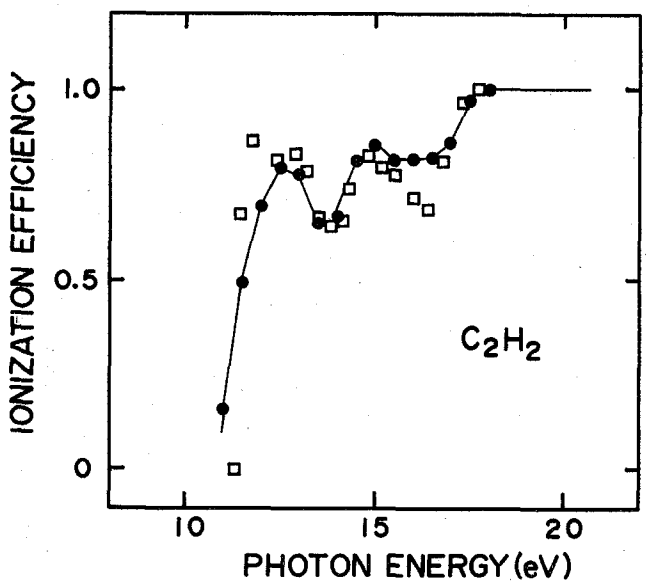

Fig. 1. Ionization efficiency of C_2H_2. □: Ref. 3 and ●: Ref. 20.

using a grating blazed at 250 nm, respectively. In these figures the relative band intensity is normalized by the CH ($\tilde{A}^2\Delta \rightarrow \tilde{X}^2\Pi_r$) emission intensity at 430 nm,[24] and is displayed after correcting the fluorescence detection efficiency of the optical system employed. The emission bands are assigned as shown in the figures. Except the $C_2(\tilde{e}^3\Pi_g \rightarrow \tilde{a}^3\Pi_u)$ transition at ~250 nm which shows a vibrational progression, the electronic transitions have been observed in the VUV photolysis of C_2H_2.[12]

When the fluorescing photofragments are produced through an ionic intermediate, thermochemically possible processes to form the CH ($\tilde{A}^2\Delta$) and $C_2(\tilde{d}^3\Pi_g)$ states, which are the lowest excited levels in the present observation, are suppoesd to be

$$C_2H_2 \rightarrow CH(\tilde{A}) + CH^+ + e^-, \quad \Delta H = 20.9 \text{ eV} \qquad (3a)$$

and

$$C_2H_2 \rightarrow C_2(\tilde{d}) + H_2^+ + e^-, \quad \Delta H = 24.2 \text{ eV} \qquad (3b)$$

where the standard heats of formation are $\Delta H_f^0(C_2H_2) = 2.35$, $\Delta H_f^0(C_2) = 8.59$, and $\Delta H_f^0(CH) = 4.95$ eV[25], and the ionization potentials of CH and H_2 are 10.46 and 15.43 eV, respectively.[24] The potential energy levels of $CH(\tilde{A})$ and $C_2(\tilde{d})$ above the groun state are taken from Ref. 24. It is clear that the photon energy of Ne(I) is insufficient for Reactions (3a) and (3b), and thus the emitting species should be formed from the superexcited state(s) of acetylene.

The fluorescence cross sections were obtained as follows: The absolute fluorescence cross section for the $N_2^+(\tilde{B}^2\Sigma_u^+ \rightarrow \tilde{X}^2\Sigma_g^+)$ transition has been reported to be 2.4 Mb (1 Mb = 10^{-18} cm^2) independent of the primary photon energy in the range of 19–24 eV.[28] We measured the dispersed spectra of the $N_2^+(\tilde{B} \rightarrow \tilde{X})$ and $CO^+(\tilde{B}, \tilde{A} \rightarrow \tilde{X})$ transitions at He(I) resonance line of 58.4 nm or 21.22 eV under the same optical conditions. By comparing the emission intensities of the $CO^+(\tilde{A})$ with that of $N_2^+(\tilde{B})$ ions, we obtained the emission cross section of 5.7 Mb for the CO^+ emission at 58.4 nm. Non-dispersed fluorescence excitation spectrum of CO^+ ion has been measured using synchrotron radiation[23], which gives a value of 0.29 as the relative emission intensity from the excited CO^+ at 16.85 eV to that at 21.22 eV. Thus, the absolute fluorescence cross section for $CO^+(\tilde{A} \rightarrow \tilde{X})$ at 16.85 eV can be deduced to be 1.6 Mb. Adopting the $CO^+(\tilde{A})$ fluorescence cross section at 16.85 eV, the total emission cross sections of C_2H_2 and C_2D_2 are obtained to be 2.3±0.1 Mb at the Ne(I) excitation. On the other hand, the total photoabsorption cross section of C_2H_2 is 37.0 Mb[20] and the ionization efficiency is $\eta_i = 0.85$ at 16.85 eV.[3,20] By multiplying these two values, the total cross section to produce the superexcited state(s) is calculated to be 5.6 Mb. This means that 40% of molecules in the superexcited state(s) of C_2H_2 decomposes into $CH(\tilde{C}, \tilde{B}, \tilde{A})$ and $C_2(\tilde{D}, \tilde{C}, \tilde{e}, \tilde{d})$ electronically excited radicals.

The fluorescence cross section for C_2H_2 presently obtained is lager than the value of ~1.5 Mb at 73.6 nm reported previously.[12] This discrepancy mainly comes from the correction of the efficiency to detect fluorescing photons. In the previous works,[12,23,27] it seems that no correction was made for the optical system used. The total photoabsorption cross section of C_2D_2 has not been reported. However, we suppose the situations of C_2D_2 are similar to those of C_2H_2.

Table 1 shows the observed emission intensity from the electronically excited state of CH and C_2 radicals. The highest emission peak is $CH(\tilde{A}\rightarrow\tilde{X})$ at 430 nm, and the strongest transition probability is $C_2(\tilde{d}\rightarrow\tilde{a})$ as judged from the accumulated area of the emission bands.

Table 1. Relative Fluorescence Intensities.

Transition	Observed Wavelength (nm)	Relative Intensity (%) C_2H_2	C_2D_2
C_2 radical			
$\tilde{D}^1\Sigma_u^+ \rightarrow \tilde{X}^1\Sigma_g^+$	225 — 238	1.5	1.2
$\tilde{e}^3\Pi_g \rightarrow \tilde{a}^3\Pi_u$	240 — 318	3.8	2.7
$\tilde{C}^1\Pi_g \rightarrow \tilde{A}^1\Pi_u$	322 — 413	20.8	19.3
$\tilde{d}^3\Pi_g \rightarrow \tilde{a}^3\Pi_u$	445 — 650	54.1	48.5
CH and CD radicals[a]			
$\tilde{C}^2\Sigma^+ \rightarrow \tilde{X}^2\Pi_r$	310 — 320	1.0	2.4
$\tilde{A}^2\Delta \rightarrow \tilde{X}^2\Pi_r$	413 — 445	18.8	25.9

a. $CH(\tilde{B}^2\Sigma^- \rightarrow \tilde{X}^2\Pi_r)$ transition at 389 nm is overlapped by the $\Delta v=0$ of $C_2(\tilde{C}\rightarrow\tilde{A})$.

A large isotope effect can be seen in the ratios of $C_2^*/CH^*=4.06$ and $C_2^*/CD^*=2.54$. Since the total fluorescence cross sections of C_2H_2 and C_2D_2 are 2.3 ± 0.1 Mb at 16.85 eV, the partial fluorescence cross sections of CH*, CD*, C_2^*(H), and C_2^*(D) radicals are deduced to be 0.45, 0.65, 1.85, and 1.65 Mb, respectively, where C_2^*(H) and C_2^*(D) denote the emitting C_2^* radicals which come from the C_2H_2 and C_2D_2 photolyses. The C_2^* radicals should be formed by the direct C-H and C-D bond

Table 2. Calculated Thresholds for Photodissociative Excitations of C_2H_2.[a]

	Process	Energy (eV)
(1)	$C_2(\tilde{d})+H_2$	8.72
(2)	$CH(\tilde{A})+CH$	10.4
(3)	$C_2(\tilde{C})+H_2$	10.5
(4)	$CH(\tilde{B})+CH$	10.7
(5)	$C_2(\tilde{e})+H_2$	11.3
(6)	$CH(\tilde{C})+CH$	11.5
(7)	$C_2(\tilde{D})+H_2$	11.6
(8)	$C_2(\tilde{d})+2H$	13.2
(9)	$C_2(\tilde{C})+2H$	15.0
(10)	$CH(\tilde{A})+C+H$	15.2
(11)	$CH(\tilde{B})+C+H$	15.5
(12)	$C(\tilde{e})+2H$	15.8
(13)	$C(\tilde{D})+2H$	16.1
(14)	$CH(\tilde{C})+C+H$	16.2

a. For electronic energy levels and the heats of formation, see Refs. 24 and 25, respectively.

fissions. Since the C-H bond energy is weaker than that of C-D, it seems normal that the emission cross section of the $C_2^*(H)$ is larger than that of $C_2^*(D)$. The calculated onsets to form the fluorescing radicals are listed in Table 2. Reaction

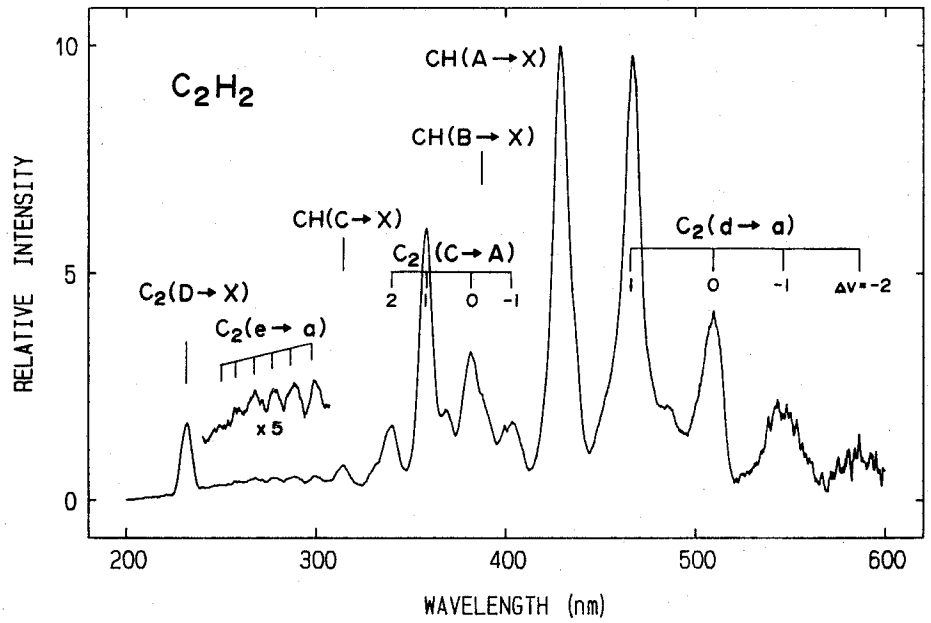

Fig. 2. Dispersed fluorescence from excitation of C_2H_2 at Ne(I). The electronic transitions of $CH(\tilde{C}, \tilde{B}, \tilde{A}\rightarrow\tilde{X})$, $C_2(\tilde{e}, \tilde{d}\rightarrow\tilde{a})$, $C_2(\tilde{C}\rightarrow\tilde{A})$, and $C_2(\tilde{D}\rightarrow\tilde{X})$ are indicated.

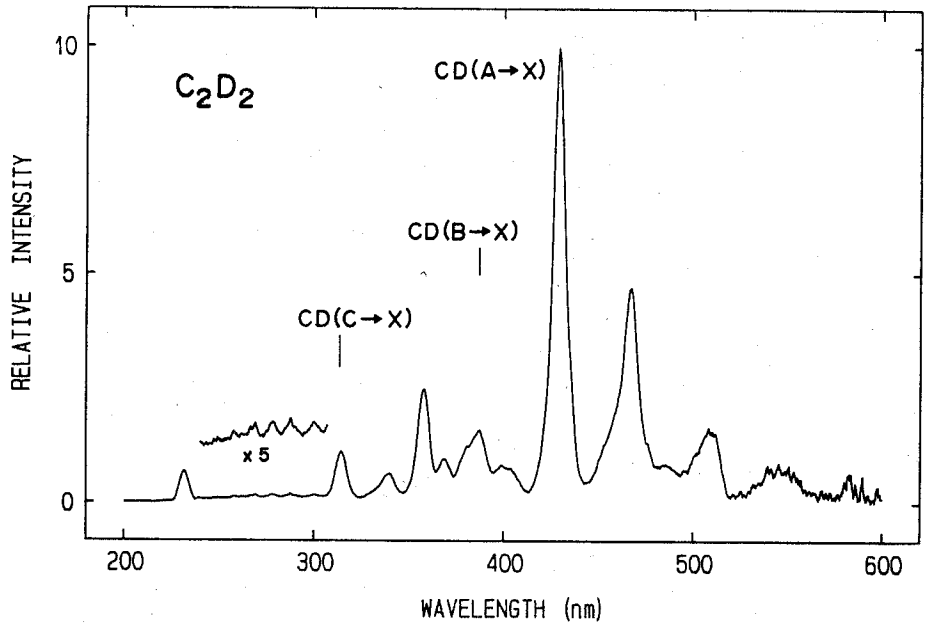

Fig. 3. Dispersed fluorescence from excitation of C_2D_2 at Ne(I).

(8) of $C_2H_2(C_2D_2) \rightarrow C_2(\tilde{d}) + 2H(2D)$ in the table has a normal isotope effect of $C_2^*(H)/C_2^*(D) = 1.12$ as seen in Figs. 2 and 3. On the other side, the partial fluorescence cross sections for the CH* and CD* suggest that the bond fission of C≡C is strongly affected by the D atom substitution, i.e., the secondary hydrogen isotope effect exceeds 40% and has an inverse tendency against the normal isotope effect.[28] When we call it in mind that the secondary isotope effects are usually quite small[28], another decomposing channel to produce non-radiative species should play an important role. That is,

$$C_2H_2 \rightarrow 2C + H_2, \quad \Delta H = 12.5 \text{ eV}. \qquad (3c)$$

Reaction (3c) contains a C≡C bond fission and should compete with the CH* producing processes such as Reactions (6) and (10) in Table 2. In C_2H_2 molecule the intramolecular H atom migration through Reaction (3c) can occur more easily than D in C_2D_2 since the tunneling effects in C_2H_2 are superior to C_2D_2. Therefore we think the intramolecular H atom migration in the superexcited C_2H_2 molecule suppresses the CH* formation and results in the large inverse isotope effect of $C_2^*/CH^* > C_2^*/CD^*$. Similar isotope effects have been observed in the dissociative excitations of CH_3CN and CD_3CN[29], CH_3OH and CD_3OD[30], and $CHCl_3$ and $CDCl_3$[31] in which non-radiative decompositions through tunnelings are suggested as discussed in the present work.

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